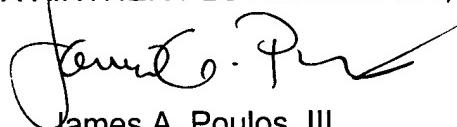


It is requested that the file of this application be marked to indicate that Applicants have complied with the requirements of 35 U.S.C. §119 and that the Patent and Trademark Office kindly acknowledge receipt of these documents.

In the event any fees are required, please charge our Deposit Account No. 01-2300.

Respectfully submitted,

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Enclosure: Italian Priority Document (1)

MINISTRY OF INDUSTRY, COMMERCE AND HANDICRAFT
GENERAL DIRECTION OF INDUSTRIAL PRODUCTION
CENTRAL PATENT OFFICE

Authentication of a copy of documents referring to the
application for a patent of the industrial invention
No. MI99.A.001516.

It is hereby declared that the attached
document is the true copy of the
original document filed together with
the above mentioned application for a
patent, the data of which result from
the enclosed filing minutes.

Rome, MAY 30, 2000

Signed for the Director
of the Department
Eng. DI CARLO

S E A L

TO THE MINISTRY OF INDUSTRY, COMMERCIAL AND HANDICRAFT
CENTRAL PATENT OFFICE - ROME
APPLICATION FOR INDUSTRIAL PATENT

AF 2101/031

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proposed class (sect., cl./subcl.)
"SYNTHESIS OF THERMOPLASTIC PERHALOGENATED (CO)POLYMERS OF
CHLOROTRIFLUOROETHYLENE"

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4)

F. PRIORITY:

priority code
country type
1) number
2) date

G. AUTHORIZED CULTURE CENTRE FOR MICROBIOLOGICAL PROCESSES name:

H. SPECIAL NOTES:

DOCUMENTATION ATTACHED:

1) RES/YES no 18 description with abstract and claims
2) RES/YES no drawing figures
3) 1 RES/YES/NO power of attorney or reference to general power MI97A 001767
4) 1 RES/YES/NO designation of inventor
5) RES/YES/NO no documents of ownership with Italian translations
6) RES/YES/NO authorisation
7) RES/YES/NO complete name of applicant
8) receipt for payment of lire 365.000= date

Certified copy of this document required? YES/NO YES

COMPILED ON 09/07/1999

THE APPLICANT(S) p. AUSIMONT S.p.A.

CONTINUATION YES/NO NO

SAMA PATENTS (ALESSANDRO RIVA)

PROVINCIAL DEPT. INO. COMM. HANICRAFT OF MI8LANO code 15

STATEMENT OF FILING: APPLICATION NO MI 99/A 001516 Reg. A

Nineteen hundred and 99 day NINE of the month of JULY

The above-mentioned applicant(s) has(have) presented to me, the undersigned, this application consisting of 00 additional pages for the granting of the above-mentioned patent.

I. NOTES OF THE DELEGATE

THE DELEGATE
Matteo Papotti

Official stamp

THE REGISTRAR
CORTONESI MAURIZIO

SYNTHESIS OF THERMOPLASTIC PERHALOGENATED (CO)POLYMERS OF
CHLOROTRIFLUOROETHYLENE

ABSTRACT

A process for the synthesis of chlorotrifluoroethylene (PCTFE) (co)polymers, containing at least 80% by moles of CTFE, being the complement to 100 one or more fluorinated monomers, preferably the complement to 100 is formed of one or more perfluorinated monomers, characterized in that the reaction medium comprises perfluoropolyoxyalkylene microemulsions wherein the fluorinated surfactant is salified with sodium and/or potassium and an inorganic potassium and/or sodium initiator.

Description of an industrial invention in the name of:
AUSIMONT S.p.A., of Italian nationality, with head office in
Milano, Piazzetta Maurilio Bossi, 3.

* * * * *

The present invention relates to halogenated polymers having good thermal stability and to the process for obtaining them.

Specifically the present invention relates to chlorotrifluoroethylene (CTFE) polymers having substantial absence of discoloration, preferably absence of discoloration, combined with a good thermal stability, and the process for their obtainment.

With chlorotrifluoroethylene (PCTFE) polymers according to the present invention, polymers containing at least 80% by moles of CTFE are intended, the complement to 100 being one or more fluorinated monomers, preferably the complement to 100 is formed of one or more perfluorinated monomers.

The polymers of the invention are to be used for obtaining pipes, sheets, films and other manufactured articles having the advantages indicated below.

More specifically it is known in the prior art that the CTFE homopolymer is a fluorinated resin having excellent chemical resistance with good properties of impermeability to gases and vapours, more specifically to oxygen, nitrogen and

water vapour, which make this resin the most suitable material for the extrusion in films to be used in the pharmaceutical packaging industry.

For the above mentioned applications, it is desirable to use a PCTFE having good thermal stability and substantial absence of discoloration allowing a wide processing window, i.e. high temperatures and residence times in extruder such that the PCTFE does not undergo discoloration without substantial weight loss. This allows to obtain articles having a more complex shape which require long residence times and high temperatures. Furthermore it is also known that the CTFE thermoplastic resins have mechanical properties which become worse when the molecular weight decreases, i.e. as the viscosity decreases. The availability of a PCTFE with a wide processing window allows the processing of polymers having a higher molecular weight and therefore to obtain articles having improved mechanical properties.

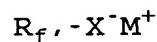
It is therefore desirable to effect an efficient industrial polymerization process, i.e. with yields not lower than about 10 g/(l×h), thermodynamically stable latexes and absence of polymer buildup in autoclave, which allows the PCTFE synthesis of different viscosity values, in particular with high molecular weights having good thermal stability combined with a substantial absence of discoloration.

The Applicant has unexpectedly and surprisingly found an efficient process for obtaining PCTFEs having high and low molecular weights and the combination of the mentioned properties.

It is therefore an object of the present invention a process for the synthesis of chlorotrifluoroethylene (PCTFE) (co)polymers, containing at least 80% by moles of CTFE, being the complement to 100 one or more fluorinated monomers, preferably the complement to 100 is formed of one or more perfluorinated monomers, characterized in that the reaction medium comprises perfluoropolyoxyalkylene microemulsions wherein the fluorinated surfactant is salified with sodium and/or potassium and an inorganic potassium and/or sodium initiator.

The perfluoropolyoxyalkylene microemulsions according to the present invention are obtainable following the methods described in USP 4,864,006, in the name of the Applicant, herein incorporated by reference.

The fluorinated surfactants of the microemulsions according to the present invention are selected from the products of general formula



wherein R_f , is a C_5-C_{14} (per)fluoroalkyl chain, or a (per)fluoropolyoxyalkylene chain, X^- is $-COO^-$ or $-SO_3^-$, M^+ is selected between Na^+ and K^+ , preferably K^+ .

According to the present invention, potassium inorganic initiators are preferred, potassium persulphate is still more preferred.

The process of the invention is carried out at a temperature between 0°C and 150°C, preferably between 10°C and 70°C. The reaction pressure is generally in the range 3-80 bar, preferably 4-20 bar.

The amount of the radical usable initiator is the standard one for the copolymerization of fluorinated olefinic monomers, and is generally in the range 0.003%-10% by weight with respect to the total amount of (co)polymerized monomers.

The control of the molecular weight of the fluorinated polymers of the invention can be carried out in various ways.

Preferred are those by a suitable dosage of the radical initiator in polymerization and the selection of the synthesis temperature. To obtain the polymers of the invention having high molecular weight, i.e. having MFI lower than 15 g/10', a low synthesis temperature (10°C-50°C) combined with a low concentration of free radicals coming from the initiator is preferred. To obtain the invention polymers having low molecular weight, i.e. having a MFI higher than 5 g/10', a high synthesis temperature (60°C-80°C) combined with a high concentration of free radicals coming from the initiator, is preferred.

Another way to control the molecular weight is the use of chain transfer agents, these can be halogenated hydrocarbons, for example chloroform or HCFC 123 and ethane or methane. The transfer agent is fed to the reactor at the beginning of the reaction, or in a continuous way or in discrete amounts during the polymerization. The used chain transfer agent amount can range within rather wide limits, depending on the reaction temperature and the molecular weight target. Generally, such amount ranges from 0.001 to 5% by weight, preferably from 0.05 to 1% by weight, with respect to the total amount of monomers fed to the reactor.

In the process according to the present invention the presence of liquid CTFE in the reaction medium, in order to obtain high productivity (R_p) in g/(l×h), is preferred.

A further object of the present invention are chlorotrifluoroethylene (PCTFE) (co)polymers, obtainable by the above described process, containing at least 80% by moles of CTFE, being the complement to 100 one or more fluorinated monomers, preferably the complement to 100 being one or more fluorinated monomers.

The chlorotrifluoroethylene (PCTFE) (co)polymers of the invention are characterized in that the CTFE homopolymer, having a MFI of about 25 g/10', does not show discoloration, as defined below, and a global very reduced weight loss

by thermogravimetric analysis.

The preferable (co)polymers of the invention are the thermoplastic ones.

The CTFE homopolymers with MFI of about 25 g/10', obtained according to the present invention, have a weight loss which is approximately the half of the weight loss of the CTFE homopolymers obtained in emulsion.

Besides the efficiency confirmation of the process object of the present invention is mainly given by the high productivity yield and by the absence of polymer buildup in autoclave.

This low weight loss of the polymers of the invention combined with absence of discoloration allows to obtain articles having a complex shape and substantial absence of defects, mainly bubbles. The presence of bubbles for example in the film extrusion, makes unusable the extruded film since the main PCTFE characteristic is the impermeability.

Among the fluorinated monomers, we can mention hexafluoropropylene, hexafluoroisobutylene, vinylidenefluoride, tetrafluoroethylene, fluorinated ethers such as perfluoroalkylvinylethers, for example perfluoroethylvinylether, perfluoromethylvinylether, preferably perfluoropropylvinyl-ether, or mixtures thereof, .

The viscosity of CTFE (co)polymers according to the pre-

sent invention is defined by the Melt Flow Index measure (MFI) at 265°C and 10 Kg load according to the ASTM D 1238-88 method.

The discoloration is determined through the observation of the strands obtained after 20, 40 and 60 minutes of residence time of the polymer in the MFI measure instrument at 265°C. Discoloration means the coloration of the extruded polymer. The product not showing discoloration is colourless or white. Polymers showing discoloration are generally yellowish or brown. The skilled in the art is able to determine whether the polymer shows or not discoloration also by using methods measuring the colour index such as for example white index or yellow index.

The thermal stability is subsequently controlled, if there is substantially no discoloration as above defined, through thermo-gravimetric measures (TGA) carried out as follows:

- i) Dynamic TGA with a heating rate of 20°C/minute up to 300°C;
- ii) Isotherm TGA at 300°C for 60 minutes.

The global variations by weight (ΔW , % by weight) and the weight loss rate in the last 10 minutes of the isothermal treatment ($\Delta W/\Delta t$, % by weight/h) are determined (see Table 1).

The perfluoropropylvinylether content in the PCTFE co-

polymers has been determined by ^{19}F -NMR.

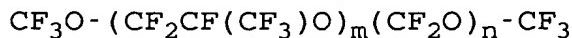
The second melting temperature (T_{2f}) and the crystallization temperature (T_{xx}) are determined by differential scanning calorimetry (DSC).

The following Examples are given for illustrative purposes and are not limitative of the present invention.

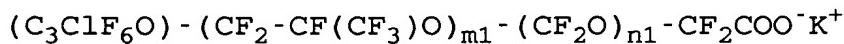
EXAMPLE 1

A 2 l AISI 316 autoclave, equipped with stirrer working at 400 rpm, has been evacuated and therein were introduced in sequence:

- 1300 g of demineralized H_2O ;
- 14 g of a microemulsion formed of: 20% by weight of Gal-den® D02, having formula:



having $m/n = 20$ and average molecular weight of 450; 40% by weight of a surfactant having formula:



having $m1/n1 = 82.7$ and average molecular weight of 527; the remaining part being formed of H_2O .

In the autoclave 400 g of CTFE were then introduced between 1°C and 5°C. Then the autoclave was heated to the reaction temperature of 60°C and 3.0 g of potassium persulphate dissolved in 90 g of demineralized H_2O were then introduced.

After 240 minutes of reaction, when the working pressure has decreased of 50% with respect to its initial value, the autoclave is vented and discharged at room temperature.

The latex discharged from the autoclave, having a concentration of 250.0 g/l of water, was cryogenically coagulated, then the polymer was separated and dried at 175°C for about 16 hours.

After the latex was discharged and the autoclave washed with water, its internal walls did not show residues.

No discoloration of the strands obtained after 60 minutes of residence time in the MFI measure instrument at 265°C, was noticed.

The test result of the thermal stability of the obtained polymer is shown in Table 1. As a further proof of the thermal stability no discoloration of the strands obtained after 80 minutes of residence time in the MFI measure instrument at 280°C, was noticed.

EXAMPLE 2 comparative (comp)

A 2 l AISI 316 autoclave, equipped with stirrer working at 400 rpm, has been evacuated and therein were introduced in sequence:

- 1200 g of demineralized H₂O;
- a solution of 5.6 g of sodium perfluorooctanoate (PFONa) in 100 g of water, corresponding to the surfactant amount

fed in Example 1.

In the autoclave 400 g of CTFE were then introduced between 1°C and 5°C. Then the autoclave was heated to the reaction temperature of 60°C and 3.0 g of potassium persulphate dissolved in 90 g of demineralized H₂O were then introduced.

After 705 minutes of reaction, when the working pressure has decreased of 50% with respect to its initial value, the autoclave is vented and discharged at room temperature.

The latex discharged from the autoclave, having a concentration of 239.0 g/l of water, was cryogenically coagulated, then the polymer was separated and dried at 175°C for about 16 hours.

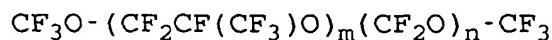
After having discharged the latex and washed with water the autoclave, its internal walls show some residues.

No discoloration of the strands obtained after 60 minutes of residence time in the MFI measure instrunent at 265°C, was noticed.

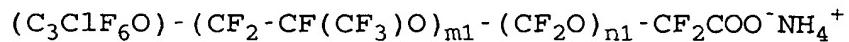
EXAMPLE 3 comparative (comp)

A 2 l AISI 316 autoclave, equipped with stirrer working at 400 rpm, has been evacuated and therein were introduced in sequence:

- 1300 g of demineralized H₂O;
- 18.3 g of a microemulsion formed of: 18.37% by weight of Galden® D02, having formula:



having m/n = 20 and average molecular weight of 450; 30.61% by weight of a surfactant having formula:



having m1/n1 = 82.7 and average molecular weight of 527, corresponding to the surfactant amount introduced in Example 1; the remaining part being formed of H₂O.

In the autoclave 400 g of CTFE were then introduced between 1°C and 5°C. Then the autoclave was heated to the reaction temperature of 60°C and 2.5 g of ammonium persulphate, equivalent by moles to the potassium persulphate of Example 1, dissolved in 90 g of demineralized H₂O were then introduced.

After 195 minutes of reaction, when the working pressure has decreased of 50% with respect to its initial value, the autoclave is vented and discharged at room temperature.

The latex discharged from the autoclave, having a concentration of 259.0 g/l of water, was cryogenically coagulated, then the polymer was separated and dried at 175°C for about 16 hours.

After the latex was discharged, part of this is present in the form of coagulum on the bottom of the autoclave.

Discoloration of the obtained strands was noticed already after 20 minutes of residence time in the MFI measure instrument at 265°C.

EXAMPLE 4 comparative (comp)

The comparative Example 3 was repeated, replacing the ammonium persulphate with 3.0 g of potassium persulphate.

After 245 minutes of reaction, when the working pressure has decreased of 50% with respect to its initial value, the autoclave is vented and discharged at room temperature.

The latex discharged from the autoclave, having a concentration of 260 g/l of water, was cryogenically coagulated, then the polymer was separated and dried at 175°C for about 16 hours.

After the latex was discharged and the autoclave washed with water, its internal walls did not show residues.

Discoloration of the obtained strands was noticed already after 20 minutes of residence time, in the MFI measure instrument at 265°C.

EXAMPLE 5 comparative (comp)

Example 1 was repeated, replacing the potassium persulphate with an equivalent amount by moles of ammonium persulphate: 2.5 g.

After 272 minutes of reaction, when the working pressure has decreased of 50% with respect to its initial value, the autoclave is vented and discharged at room temperature.

The latex discharged from the autoclave, having a concentration of 275 g/l water, was cryogenically coagulated,

then the polymer was separated and dried at 175°C for about 16 hours.

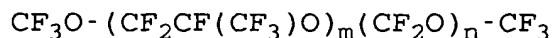
After the latex was discharged and the autoclave washed with water, its internal walls did not show residues.

Discoloration of the obtained strands was noticed already after 20 minutes of residence time in the MFI measure instrument at 265°C.

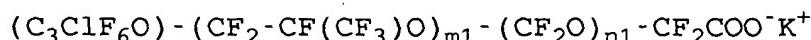
EXAMPLE 6

A 2 l AISI 316 autoclave, equipped with stirrer working at 400 rpm, has been evacuated and therein were introduced in sequence:

- 1200 g of demineralized H₂O;
- 14 g of a microemulsion formed of: 20% by weight of Gal-den® D02, having formula:



having m/n = 20 and average molecular weight of 450; 40% by weight of a surfactant having formula:



having m1/n1 = 82.7 and average molecular weight of 527; the remaining part being formed of H₂O

- 3.0 g of potassium persulphate dissolved in 200 g of demineralized H₂O.

In the autoclave 33 g of perfluoropropylvinylether (FPVE) and 400 g of CTFE were then introduced between 1°C and 5°C.

Then the autoclave was heated to reaction temperature of 50°C.

After 500 minutes of reaction, when the working pressure has decreased of 50% with respect to its initial value, the autoclave is vented and discharged at room temperature.

The latex discharged from the autoclave, having a concentration of 268 g/l of water, was cryogenically coagulated, then the polymer was separated and dried at 175°C for about 16 hours.

The perfluoropropylvinylether content in the obtained copolymer is 1.5% by moles.

After the latex was discharged and the autoclave was washed with water, its internal walls did not show residues.

No discoloration of the obtained strands was noticed after 60 minutes of residence time in the MFI measure instrument at 265°C.

EXAMPLE 7 comparative

A 2 l AISI 316 autoclave, equipped with stirrer working at 400 rpm, has been evacuated and therein were introduced in sequence:

- 1200 g of demineralized H₂O;
- a solution of 5.6 g of sodium perfluorooctanoate (PFONa) in 100 g of water, corresponding to the surfactant amount introduced in Example 1.

- 3.0 g of potassium persulphate dissolved in 200 g of demineralized H₂O.

In the autoclave 33 g of perfluoropropylvinylether (FPVE) and 400 g of CTFE were then introduced between 1°C and 5°C. Then the autoclave was heated to the reaction temperature of 50°C.

After 1890 minutes of reaction, when the working pressure has decreased of 50% with respect to its initial value, the autoclave is vented and discharged at room temperature.

The latex discharged from the autoclave, having a concentration of 239 g/l in water, was cryogenically coagulated, then the polymer was separated and dried at 175°C for about 16 hours.

After the latex was discharged and the autoclave washed with water, its internal walls are completely covered by a layer of the obtained polymer.

Discoloration of the obtained strands was noticed already after 60 minutes of residence time in the MFI measure instrument at 265°C.

TABLE 1

EXAMPLE	1	2 (comp)	6	7 (comp)
T_{2f} ($^{\circ}$ C)	212.2	211.4	197.1	--
T_{xx} ($^{\circ}$ C)	181.7	175.5	162.0	--
R_p (g/(l×h))	62.5	20.3	32.2	7.6
MFI(g/10')	25.0	24.6	9.8	4.9
ΔW (% w)	0.34	0.81	--	--
$\Delta W/\Delta t$ (% w/h)	0.126	0.312	--	--
DISCOLORATION	NO	NO	NO	YES

CLAIMS

1. A process for the synthesis of chlorotrifluoroethylene (PCTFE) (co)polymers, containing at least 80% by moles of CTFE, the complement to 100 being one or more fluorinated monomers, preferably the complement to 100 is formed of one or more perfluorinated monomers, characterized in that the reaction medium comprises perfluoropolyoxyalkylene microemulsions wherein the fluorinated surfactant is salified with sodium and/or potassium and an inorganic potassium and/or sodium initiator.
 2. A process according to claim 1 wherein the fluorinated surfactant is selected from the products of general formula
- $$R_f, -X^- M^+$$
- wherein R_f , is a C_5-C_{14} (per)fluoroalkyl chain, or a (per)fluoropolyoxyalkylene chain, X^- is $-COO^-$ or $-SO_3^-$, M^+ is selected between Na^+ and K^+ .
3. A process according to claim 2 wherein M^+ is preferably K^+ .
 4. A process according to claims 1-3 wherein potassium inorganic initiators are preferred.
 5. A process according to claim 4 wherein the potassium inorganic initiator is potassium persulphate.
 6. A process according to claims 1-5 wherein the temperature

is in the range 0°C-150°C and the pressure is in the range 3-80 bar.

7. A process according to claim 6 wherein the temperature ranges between 10°C and 70°C and the pressure between 4 and 20 bar.
8. A process according to claims 1-7 wherein the presence of liquid CTFE in the reaction medium is preferred.